MONITORING STUDY FOR TRIBUTYLTIN CONTAMINATION IN CALIFORNIA LAKES, 1987

By

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and

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June, 1989

Environmental Hazards Assessment Program

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ABSTRACT

Tributyltin (TBT) is the active ingredient in antifouling paints used on boat hulls, docks and fish nets to prevent the growth of aquatic organisms. Tributyltin is both acutely and chronically toxic to a wide range of non-target aquatic organisms in concentrations ranging from 0.02 - $\geq$0.2 parts per billion and can pose a serious threat to aquatic environments. Although the presence of TBT in coastal waters of California has been well documented, very little is known about the extent of TBT contamination in fresh water lakes. The high concentrations of TBT present in coastal waters prompted agencies of the California Department of Fish and Game (CDFG) and the California Department of Food and Agriculture (CDFA) to design a two phase study to document the presence of TBT in fresh water lakes.

In the first phase, the ten fresh water marinas in the State with the largest boating capacities were selected for the collection of surface water samples to ascertain the range of TBT concentrations in these high use areas. Surface water samples were collected from 10 marinas on 6 lakes. The TBT concentrations of the samples ranged from none detected (detection limit 17 ng/L) to 1220 ng/L. The marina with the highest TBT concentrations detected was selected for further sampling to determine the TBT concentrations in water, sediment and biota within the marina, and to investigate the extent of TBT movement into the lake environment.

The second phase of sampling took place at Tahoe Keys Marina on Lake Tahoe. Surface and bottom water, sediment, and biota samples were collected at a total of five locations inside and outside the marina. Tributyltin concentrations in water ranged from 340 to 1400 ng/L, in sediment from 430 to 1400 ng/g (dry weight), and in fish from 250 to 4800 ng/g (fresh weight). TBT was not detected [detection limit 24 ng/L for water and 12 ng/g (dry wt.) for sediment] in water or sediment samples collected in the lake outside the marina. However, fish samples from the same open water sites contained up to 600 ng/g fresh weight TBT.

The concentrations observed in the water of this marina exceed the Environmental Protection Agency's chronic toxicity value for the ambient aquatic life water quality advisory of 30 ng/L TBT in fresh water. Recent legislation and regulations enacted by the State should greatly reduce the use of TBT containing paints. These regulations are expected to substantially reduce the source of contamination and eventually environmental residues. The Tahoe Keys Marina will be periodically monitored to determine the effectiveness of the regulations in reducing environmental and biotic TBT residues.

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I. INTRODUCTION

Tributyltin (TBT) is the active ingredient in antifouling paints used on boat hulls, docks, fish nets and other structures to prevent the growth of aquatic fouling organisms (barnacles, algae, etc.). The formulation of these paints maintains pesticidal properties by continuously leaching TBT into the water/paint interface. Three formulations of antifoulant paints have been developed, each having a characteristic leaching pattern and release rate. Additional sources of TBT contamination are attributed to paint chips and spent abrasive dusts from boat repair yards.

Tributyltin has been used in antifouling paints since the 1960's with additional formulations being developed in the 1970's. Tributyltin compounds registered for use in paints are: bis(tributyltin) oxide, bis(tributyltin) adipate, bis(tributyltin) sulfide, bis(tributyltin) dodecenyl succinate, tributyltin flouride, tributyltin acrylate, tributyltin acetate, tributyltin methacrylate and tributyltin resinate.

Concern for the presence of TBT in the aquatic environment is due to its extreme toxicity to a wide range of non-target aquatic organisms (1,2,3,4). Tributyltin is both acutely and chronically toxic to gastropods, bivalves, crustaceans, algae and fish in concentrations ranging from 0.02 - $\geq$0.2 parts per billion (ppb) (1,4). Because this chemical has the potential to cause severe impacts on aquatic biota, the California Department of Fish and Game (CDFG) and the California Department of Food and Agriculture (CDFA) sought to assess the presence of TBT in fresh water lakes of California.

The presence of TBT in the coastal waters and estuaries of California has been well documented (1,5,6). However, very little information is available pertaining to the amount of TBT contamination in California's fresh water lakes. Therefore, the Pesticide Investigations Unit (PIU) of the CDFG in conjunction with the Environmental Hazards Assessment Program (EHAP) of the CDFA designed a two phase study to document the presence of TBT in fresh water lakes. The initial Phase I surveyed marinas with high boating traffic to ascertain the range of TBT concentrations in high use areas. The marina with highest TBT concentrations detected in Phase I was selected for Phase II sampling to determine the TBT concentrations in water, sediment and biota present within the marina and to investigate the extent of TBT movement into the lake environment.

Tributyltin- Environmental Degradation

Once dissolved in water, TBT appears to degrade by a process of stepwise debutylation to dibutyltin, monobutyltin and finally to inorganic tin. Toxicity also decreases with decreasing butyl groups (3,7).

The most important pathways of TBT degradation in water and sediment are from biological metabolism including microbes, oligochaetes, algae and vertebrates, and from photolysis (2,8). The photochemical degradation half-life of TBT in fresh water has been estimated to be a minimum of 3 months, with the rate and degree of photolysis being dependent on sunlight intensity and depth of light penetration into the water column (8,9). Biological degradation half-life can range from 1 to 2 weeks under aerobic conditions to over a year under anaerobic conditions (4). The half-life of TBT in water at 20°C has been reported as 5 months and 4 months in a sediment-water mixture (8). Volatilization is not considered to be a significant degradation pathway (9).

II. MATERIALS AND METHODS

Study Design

Phase I - To conduct the initial phase of the study, the CDFG identified six lakes with marinas having the highest number of boat slots (Table 1) (10). Three natural lakes (Lake Tahoe, Clear Lake and Big Bear Lake) and three reservoirs (Clair Engle Lake, Lake Berryessa and Millerton Lake) were represented in the initial selection (Figure 1). Surface water samples were collected from the selected marinas on each of these lakes in August, 1987.

Phase II - Results from the initial Phase I identified Tahoe Keys Marina on Lake Tahoe as having the highest TBT concentrations in water. Therefore, Phase II monitoring was implemented at this marina. Five sampling sites (Figure 2) inside and outside the marina were selected for the collection of water and sediment by the EHAP, and for biota samples by the PIU. Throughout this report site 1 refers to the area in the backwaters of the marina, site 2 is the area inside the marina immediately adjacent to the inlet channel, site 3 is an area in the lake approximately 450 meters north of the marina inlet, site 4 is an area approximately 900 meters north of the marina inlet, and site 5 is next to the inlet within a large residential marina that is adjacent to Tahoe Keys Marina (Figure 2). All Phase II samples were collected in September, 1987.

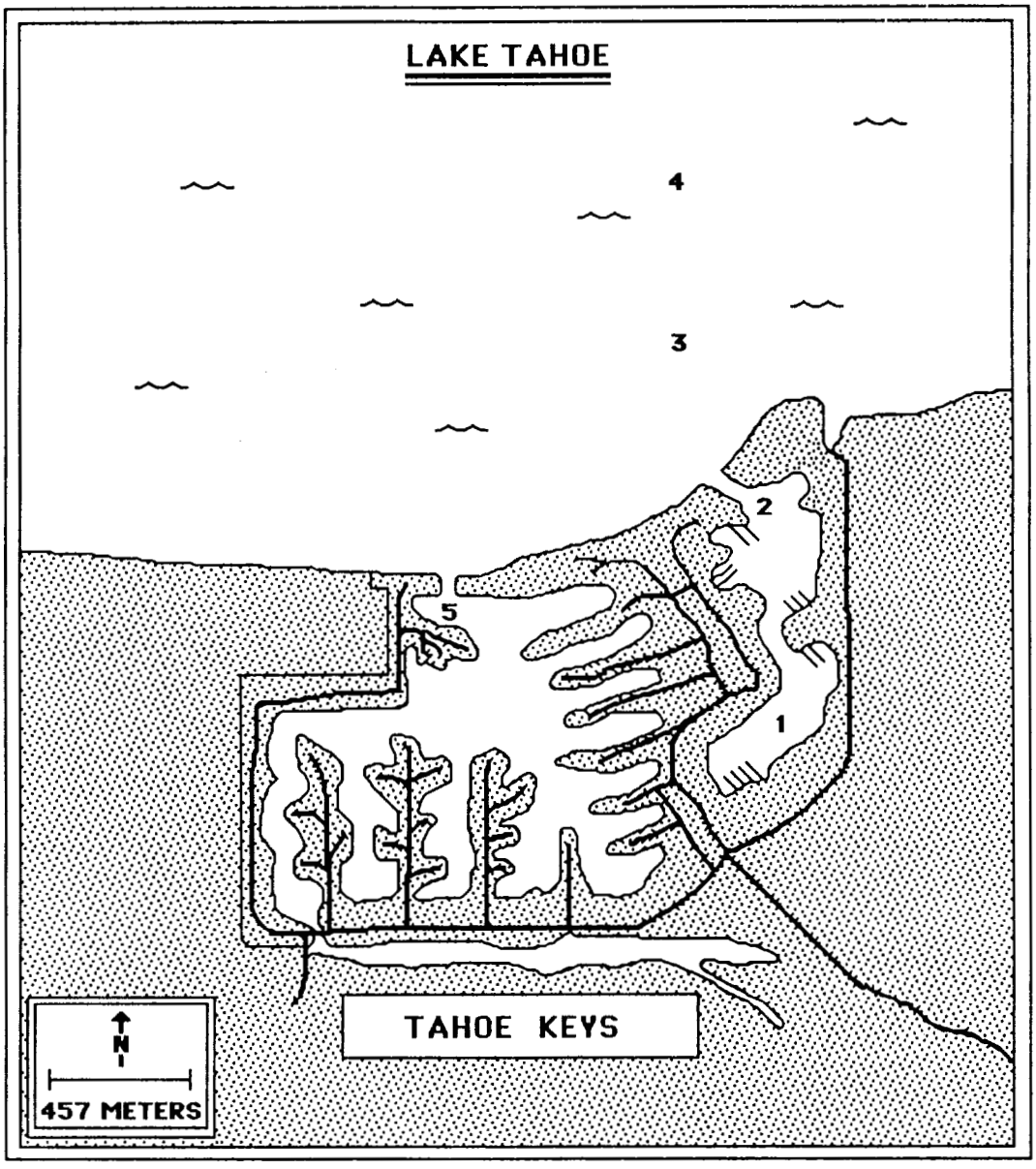
Sampling Methods

Phase I - Surface water samples for the initial phase were collected from docks centrally located within the selected marinas. Water samples were collected by

Table 1. Lakes surveyed and boat capacity of marinas sampled in Phase I, 1987 TBT study (10).

Lake	Marina	Capacity
Reservoirs		
Clair Engle Lake	A	150
Lake Berryessa	B	290
	C	350
Millerton Lake	D	500
Natural Lakes		
Clear Lake	E	150
	F	94
Lake Tahoe	G	133
	H	120
	I	160
Big Bear Lake	J	500

Figure 1. Location of lakes sampled in Phase I of TBT Study, August, 1987.



SAMPLES COLLECTED

SITE	SURFACE WATER	BOTTOM WATER	SEDIMENT	BIOTA
1	X	X	X	X
2	X	X	X	X
3	X	X		X
4	X	X	X	X
5	X			

FIGURE 2. LOCATION OF TRIBUTYLTIN MONITORING SITES (1-5) AND SAMPLES COLLECTED IN THE TAHOE KEYS MARINA AREA, LAKE TAHOE, SEPTEMBER, 1987.

submerging an inverted 7.5 liter polycarbonate carboy to a depth of approximately 25 cm. The container was rotated to allow it to fill and then removed from the water. Water from the carboy was split into two 1-liter polycarbonate bottles. The bottles were sealed with teflon-lined lids and stored on dry ice for transport to the laboratory. One bottle from each site was sent to the CDFG Water Pollution Control Laboratory and the other split sample was sent to the Moss Landing Marine Laboratory for analysis. An additional replicate water sample was also collected at each site by submerging an inverted 1-liter polycarbonate bottle, rotating it, and allowing it to fill. The bottle was then removed from the water and treated as described for the split samples. All replicate water samples were analyzed by the CDFG laboratory. All water samples remained frozen until prepared for analysis. Water temperature and pH were recorded at each sampling site at each marina. All sampling equipment was washed with detergent, rinsed in tap water and then in distilled water between sample sites.

Phase II - Surface Water: Samples were collected at each site (Figure 2). Water samples were collected in one-liter polycarbonate bottles submerged to a depth of approximately 25 cm and allowed to fill as previously described. The bottles were sealed with teflon lined-lids, stored on dry ice and transported to the CDFG laboratory for analysis.

Bottom Water: Samples were collected at sites 1, 2 and 3 with a sampling device that consisted of a polycarbonate bottle attached to a line 38 cm above a 4 kg weight. A neoprene stopper attached to a secondary line was placed in the bottle mouth. The bottle and weight were lowered by hand to the desired depth. The bottle remained vertical underwater due to its buoyancy with the top up and stopper in place. The stopper was pulled out allowing the bottle to fill

resulting in the bottle opening to become oriented in a downward position. The bottle was then raised in the inverted position. The cap was placed on the bottle while still submerged and the bottle removed from the water. Scuba divers were used to collect the samples at site 4. Sample bottles were sealed with teflon-lined lids, stored on dry ice and transported to the CDFG laboratory for analysis. All water samples remained frozen until prepared for analysis.

Water temperature, depth, and pH were recorded for both surface and bottom water samples collected at each sampling site (Appendix II, Table II-1).

Sediment: Samples were collected at sites 1 and 2 with a Wildco Instrument sediment sampler (Model 2321-A10). The sampler was held above the surface of the water and released causing it to be embedded in the bottom substrate. An attached rope was used to retrieve the sampler. Sediment samples at site 4 were collected by scuba divers that hand drove the sample barrel into the sediment, then returned to the surface with the sediment in the barrel. The top 10 cm of the core was placed in polycarbonate jars and sealed with teflon-lined lids. The samples were placed on dry ice and transported to CDFG Water Pollution Laboratory for analysis. Sampling equipment was cleaned as previously described between each site.

Biota Samples: Tahoe sucker Catostomus tahoensis, tui chub Gila bicolor, rainbow trout Salmo gairdneri, brown trout Salmo trutta and crayfish Procambarus sp. were collected at monitoring sites 1, 2, 3 and 4 in Lake Tahoe. At sites 1, 2 and 3, baited minnow and crayfish traps were set on 10 common lines with minnow traps 2 to 3 feet from the surface and crayfish traps on the bottom. At sites 2, 3 and 4, variable size monofilament gill nets were set at the bottom. Sampling equipment was left overnight and the animals (Appendix I) were removed

from the traps the following morning, placed in plastic bags with sampling location cards, put on dry ice and then transported to the CDFG laboratory where they remained frozen until prepared for analysis.

The frozen animals were thawed overnight at room temperature prior to analysis. Fish from each location were composited by species and size into groups of three individuals to produce replicate samples of approximately equal weight (Table 2). Crayfish were put into groups of six individuals. Skeletal muscle from fish and telson from crayfish were removed with a stainless steel fillet knife. Samples were homogenized in a stainless steel blender. The homogenate was deposited in 250-ml borosilicate glass containers and refrozen until analysis. The blender and utensils were cleaned after each use by washing in hot soapy water followed by rinsing in deionized water and then by rinsing in a mixture of Nanograde hexane and Nanograde acetone (1 + 1). The borosilicate glass containers were cleaned by the same procedure prior to use.

Analytical Methods

The CDFG Water Pollution Control Laboratory was the primary laboratory that conducted analysis on all water, sediment and biota samples for both study phases. Tributyltin and DBT concentrations in all sample types were determined by flame photometric gas chromatography using variations of Tsuda et al (11) and Matthias et al (12). Detailed descriptions of these analytical methods are contained in Appendix III. The Moss Landing Marine Laboratory in Monterey County was the quality control laboratory for the Phase I samples. Water samples were analyzed for TBT and DBT using atomic absorbtion spectrophotometry as described by Valkirs et al (13) and Stallard et al (14). The U.S. Navy Laboratory in San Diego was the quality control laboratory for Phase II. Water and sediment were

Table 2. Species and number of animals used to prepare replicate and quality control (QC) samples of Lake Tahoe biota collected September 29, 1987, Tributyltin Monitoring Study, Lake Tahoe, California.

			CDFG Laboratory		Navy Laboratory	
Site	Species	No. of Animals/Sample	No. of Samples	Type	No. of Samples	Type
1	Tahoe sucker	3	1			
1	Tui chub	3	1			
1	Crayfish	6	1			
2	Tahoe sucker	3	5	replicate		
2	Tahoe sucker	--[a]	5	intralab QC		
2	Tahoe sucker	6	2	interlab split	2	interlab split
2	Tui chub	3	5	replicate		
2	Tui chub	--[a]	5	intralab QC		
2	Rainbow trout	3	1	interlab split	1	interlab split
3	Tahoe sucker	3	5	replicate		
3	Tui chub	3	5	replicate		
3	Tui chub	--[a]	2	interlab split	2	interlab split
4	Tahoe sucker	3	3	replicate		
4	Tui chub	3	3	replicate		
4	Crayfish	6	1			
4	Brown trout	1	1			

[a]These samples were produced from one-half of the volume from each of the five replicate tissue samples, composited, rehomogenized, and split into quality control samples for analysis.

analyzed for TBT and DBT concentrations using similar methods (13,14). Flame photometric gas chromotography was used for biota sample analysis using the method described by Cola and Dooley (15).

Quality Control Samples

Phase I - The water samples sent to the Moss Landing Marine laboratory as previously mentioned were for the purpose of quality control. A total of 11 samples were submitted to the quality control laboratory.

Phase II - For purposes of quality control, additional surface water was collected in a 7.5 gallon polycarbonate carboy and split into seven 1-liter polycarbonate bottles, sealed and stored on dry ice. Sediment plugs of sufficient quantity were collected, mixed in a polycarbonate carboy, split into seven polycarbonate jars, sealed and stored on dry ice. Replicate homogenate biota samples of sufficient quantity were composited, rehomogenized and split into several clean borosilicate glass jars, sealed, and refrozen until analyzed. Chemical analyses on all split samples were performed by the U.S. Navy Laboratory in San Diego and the CDFG Water Pollution Control Laboratory. Split tissue aliquots were produced from biota samples for purposes of intralaboratory quality control by the CDFG Water Pollution Control Laboratory in addition to the interlaboratory split samples.

Statistical Methods

Phase I - This was a qualitative survey and statistical inferences from these data are inappropriate. Therefore, formal statistical calculations were not performed.

Phase II - Mean water and sediment sample concentrations of TBT and DBT were estimated assuming an underlying two parameter, log-normal distribution (16,17). The means and standard deviations were calculated using the minimum variance unbiased estimators developed by Finney (18) and Sichel (19).

If a collection of samples taken at a particular location and depth contained one or two samples below the analytical detection limit, then statistical methods for censored datasets were employed. Due to the small sample sizes (n=4), maximum likelihood methods did not apply. The distributional parameters, mean and standard deviation, were calculated using the best linear estimates of Gupta (20) which are appropriate even with small sample sizes (21). If more than two of the four samples were determined to be below the detection limit, then no calculations were performed due to insufficient information.

Comparison of butyltin concentrations in water between lake locations and depth were carried out using the non-parametric technique of two-way analysis of variance on ranks (22,23). For purposes of statistical analyses, values below the detection limit were first assigned the value of the minimum detectable limit (24 and 40 nanograms per liter (ng/L) for TBT and DBT water samples, respectively) prior to the assignment of ranks. Sediment sample locations were compared using the Wilcoxon rank-sum test. For sediment samples below the minimum detection limit, the values of 12 and 20 nanograms per gram (ng/g) were used for TBT and DBT respectively.

Mean and standard deviations for biota data were calculated using the censored data technique as previously described. Mean TBT and DBT residues in sucker and chub tissue at site 2, site 3 and site 4 were compared using non-parametric Kruskal-Wallis test based on ranks.

III. RESULTS

Phase I - The analytical results of Phase I are presented in Table 3. Tributyltin concentrations in water ranged from 17 to 1220 ng/L and DBT from 176 to 686 ng/L. Tributyltin was detected in 4 lakes and DBT in only 1. These data show Tahoe Keys Marina on Lake Tahoe to have substantially higher TBT concentrations than any of the other marinas sampled.

Phase II - Water: Results from the chemical analyses of the water samples for TBT and DBT are summarized in Table 4. A complete listing of sample results is given in Appendix II, Table II-1.

The highest concentrations of TBT and DBT were found at the Tahoe Keys Marina dock area (site 1) followed by the marina inlet (site 2). No detectable concentrations were found at sites 3 and 4 in the open water of Lake Tahoe. Only one of the water samples collected at the residential area of the Tahoe Keys (site 5) contained measurable amounts of TBT.

Although no differences in TBT or DBT were detected between depths at which the samples were taken, significant differences were measured between site 1 and site 2 locations ($P < 0.01$). Tributyltin concentrations at site 1 ranged from 340 to 1400 ng/L with mean values of 738 ng/L and 728 ng/L for samples taken from the surface and bottom, respectively. At site 2, TBT concentrations ranged from 41 to 140 ng/L with mean values of 96 and 75 ng/L for surface and bottom samples, respectively.

At site 1, DBT concentrations ranged from none-detected to 94 ng/L with mean concentrations of 71 and 76 ng/L for the surface and near bottom water samples,

Table 3. Tributyltin (TBT) and dibutyltin (DBT) concentrations in replicate water samples collected from ten marinas on six lakes in California, August, 1987.

Lake	Marina	pH	Water Temp. C°	Rep.	TBT	DBT
					ng/L	
Reservoirs						
Clair Engle Lake	A	7.1	22	1	ND[a]	ND
				2	ND	ND
Lake Berryessa	B	8.5	21	1	ND	ND
				2	17	ND
	C	8.4	25	1	ND	ND
				2	ND	ND
Millerton Lake	D	7.1	25	1	17	ND
				2	ND	ND
Natural Lakes						
Clear Lake	E	7.9	22	1	34	ND
				2	20	ND
	F	8.5	22	1	17	ND
				2	17	ND
Lake Tahoe	G:1[b]	8.9	19	1	1220	690
				2	950	390
	G:2	8.5	19	1	660	180
				2	1000	370
	H	6.7	15	1	63	ND
				2	93	ND
	I	7.0	15	1	46	ND
				2	78	ND
Big Bear Lake	J	7.1	20	1	17	ND
				2	ND	ND

[a]ND= none detected; minimum detection limits for TBT and DBT were 17 ng/L (ppt) and 33 ng/L (ppt), respectively.

[b]Samples were collected from two areas within the marina, G:1 was located in the rear area near Site 1 as shown in Figure 2, and G:2 was in the front area near Site 2 as shown in Figure 2.

Table 4. Mean butyltin concentrations in water samples collected from five monitoring stations in Lake Tahoe, September, 1987. See Figure 2 for locations of sites.

Site	Depth	TBT N	TBT Mean[a]	TBT SD[b]	DBT Mean	DBT SD
			ng/L			
Site 1						
Tahoe Keys Marina	Surface	4	738	420	71	29
	Bottom	4	728	115	76	20
Site 2						
Tahoe Keys	Surface	4	96	27	IS[c]	-
Marina Inlet	Bottom	4	75	30	ND[d]	-
Site 3						
Lake Tahoe	Surface	4	ND	-	ND	-
	Bottom	4	ND	-	ND	-
Site 4						
Lake Tahoe	Surface	4	ND	-	ND	-
	Bottom	4	ND	-	ND	-
Site 5						
Tahoe Keys Residential Marina	Surface	4	IS	-	IS	-

[a] In the case of samples below the minimum detectable limit, means and standard deviations on a logarithmic scale were calculated using best linear estimates of Gupta. Back transformations from the logarithmic scale were calculated using minimum variance unbiased estimators (see statistical references for greater detail).

[b] SD= standard deviation.

[c] Insufficient information; measurable contaminant information in only one of the four samples. See Appendix II, Table II-1 for greater detail.

[d] None detected. All samples collected contained no measurable amount of butyltin compounds. Minimum detection limit of 24 and 40 ng/L (ppt) for TBT and DBT, respectively.

respectively. All other water samples were analyzed as having no measurable amounts of DBT except for one surface water sample collected at the inlet to the Tahoe Keys marina. This sample was measured as containing 100 ng/L of DBT.

Sediment: Results from the chemical analyses for TBT and DBT are summarized in Table 5. A complete listing of sample results is shown in Appendix III, Table II-2.

Measurable amounts of TBT and DBT were detected at site 1 and at site 2. No measurable amounts of butyltin were found in the sediment samples collected at site 4.

Sediment samples collected at site 1 showed significantly higher TBT and DBT concentrations than those samples taken at the inlet to the marina ($p \leq 0.05$). Mean TBT residues in sediment at site 1 were 775 ng/g (dry weight) of TBT compared with 141 ng/g (dry weight) for samples taken at site 2. Dibutyltin results followed a similar trend with a mean concentration of 590 ng/g (dry weight) at site 1 and 106 ng/g (dry weight) at site 2.

Biota: Tributyltin and DBT residues in fish from the Tahoe Keys Marina ranged from 100 to 4800 and 20 to 840 ng/g (fresh weight), respectively (Table 6). A complete listing of sample results is shown in Appendix II, Table II-3. Site 2 had significantly ($p \leq 0.05$) higher residues of TBT in both sucker and chub tissue then did site 3 and 4; no significant differences were detected in DBT residues among the other sites. Site 1 had only one sample per species so statistical comparison to other sites could not be performed.

Table 5. Mean butyltin concentrations in sediment samples collected from three monitoring stations in Lake Tahoe, September, 1987. See Figure 2 for locations of sample sites.

Site	Depth in Meters	N	TBT Mean[a]	TBT SD	DBT Mean	DBT SD
			ng/g, dry weight			
Site 1						
Tahoe Keys Marina	3.7	4	775	398	590	347
Site 2						
Tahoe Keys	3.7	4	141	51	106	64
Site 4						
Lake Tahoe	13.0	4	ND[b]	-	ND	-

[a] In the case of samples below the minimum detectable limit, means and standard deviations on a logarithmic scale were calculated using best linear estimates of Gupta. Back transformations from the logarithmic scale were calculated using minimum variance unbiased estimators. (See statistical references for greater detail.)

[b] None detected; minimum detection limit of 12 and 20 ng/g (ppb) for TBT and DBT, respectively. See Appendix II, Table II-2 for greater detail.

Table 6. Mean tributyltin (TBT) and dibutyltin (DBT) concentrations, standard deviations (SD), range, number of samples and number of animals per sample for biota collected at Tahoe Keys Marina, South Lake Tahoe, September, 1987. See Figure 2 for locations of sample sites.

Sample Type	No. of Samples	No. of Animals per Sample	TBT			DBT		
			Mean	SD	Range	Mean	SD	Range
			ng/g, fresh weight					
Site 1								
Sucker	1	3	4800	NA[a]	NA	840	NA	NA
Chub	1	3	1300	NA	NA	500	NA	NA
Crayfish	1	6	ND[b]	NA	NA	ND	NA	NA
Site 2								
Sucker	5	3	1100	460	480-1600	28	7	ND-37
Chub	5	3	1300	740	580-2200	120	100	ND-220
Site 3								
Sucker	5	3	94	64	ND-290	ND	NA	NA
Chub	5	3	350	180	110-600	40	21	20-72
Site 4								
Sucker	3	3	140	160	ND-290	ND	NA	NA
Chub	3	3	290	160	140-460	62	20	40-78
Trout	1	1	100	NA	NA	ND	NA	NA
Crayfish	1	6	ND	NA	NA	ND	NA	NA

[a]Not applicable, only one sample.

[b]None detected; minimum detection limits for TBT and DBT were 12 and 20 ng/g (fresh weight), respectively.

Quality Control Results

Phase I - Quality control results for Phase I are presented in Table 7. Results for seven of the eleven samples submitted were available for this report. For those split samples where both laboratories found TBT above detection limit, Moss Landing Laboratory was 105% of those reported by the Water Pollution Control Laboratory.

Phase II - Concentrations of TBT and DBT in split water samples determined by the Navy were 140% and 220% higher, respectively, than in CDFG samples (Table 8). The Navy's TBT determinations were 64% higher for rainbow trout, 30% lower for tui chub and equal for Tahoe sucker (Table 8). Determinations of DBT for split tissue samples were not consistently detected by both laboratories. In addition, the sample size was too small to make comparisons. Split sediment sample results from the Navy were not available so the split sediment results from the CDFG were treated as intralaboratory quality control data. All intralaboratory quality control results are presented in Table 9.

IV. DISCUSSION

Toxicity Review

Limited data exists regarding the toxicity of TBT to fresh water biota. A literature survey conducted by CDFG detected many inadequacies and inconsistencies in the methods used in deriving toxicity values. The United States Environmental Protection Agency (EPA) using "Guidelines for Deriving Numerical National Water Quality Criteria for the Protection of Aquatic Organisms and Their Uses" (24) evaluated acceptable acute and chronic toxicity data and derived final acute (300 ng/L) and chronic (26 ng/L) values for TBT in fresh

Table 7. Interlaboratory split water sample results conducted by the CDFG and Moss Landing Marine Laboratory for TBT in Phase 1 samples.

Lake	Marina	TBT	
		CDFG	MLML
		ng/L	
Clair Engle Lake	A	ND[a]	NR[b]
Lake Berryessa	B	ND	23
	C	ND	NR
Millerton Lake	D	17	32
Clear Lake	E	34	48
	F	17	56
Lake Tahoe	G:1[c]	1220	1240
	G:2	660	NR
	H	63	56
	I	46	35
Big Bear Lake	J	ND	NR

[a]ND= none detected; minimum detection limits for TBT were 17 ng/L for CDFG Laboratory. No minimum detection limit was stated for Moss Landing Marine Laboratory.

[b]NR= no results; sample results not available for this report.

[c]Samples were collected from two areas within the marina, G:1 was located in the rear area near Site 1 as shown in Figure 2, and G:2 was in the front area near Site 2 as shown in Figure 2.

Table 8. Results of interlaboratory split biota and water samples conducted by the California Department of Fish and Game (CDFG) and the Navy for tributyltin (TBT) and dibutyltin (DBT). All samples collected at Tahoe Keys Marina, South Lake Tahoe, September, 1987.

Sample Typle	Number of Samples	TBT Mean	TBT Range	DBT Mean	DBT Range
		ng/g, fresh weight			
Sucker					
CDFG	2	1150	1100-1200	ND[a]	-
Navy	2	1190	970-1400	ND	-
Chub					
CDFG	2	470	430-480	40	36-42
Navy	2	330	320-330	ND	-
Trout					
CDFG	1	250	-	ND	-
Navy	1	410	-	ND	-
		ng/L			
Water					
CDFG	4[b]	350	220-620	-[c]	-
Navy	2	680	620-730	160	140-190

[a]None detected; minimum detection limits (MDL) for TBT and DBT analysis conducted by the CDFG were 24 and 40 ng/L (ppt) respectively in water, and 12 and 20 ng/g, (fresh weight, ppb) respectively in tissue. Minimum detection limit for TBT and DBT analysis conducted by the Navy was 5 ng/L (ppt) in water, no information was available for the MDL in tissue.

[b]One outlier value was discarded before calculating mean.

[c]Only one of the five samples analyzed contained a detectable level of DBT at 100 ng/L.

Table 9. Intralaboratory quality control results of split samples produced by CDFG from samples collected at Tahoe Keys Marina, South Lake Tahoe, September, 1987. Results expressed as mean concentrations of TBT (tributyltin) and DBT (dibutyltin), standard deviation (SD), coefficient of variation (CV%) and number of duplicates (N).

Sample Type	N	TBT				DBT			
		Mean	SD	Range	CV%	Mean	SD	Range	CV%
		ng/g				ng/g			
Sediment[a]	5	210	24	180-240	11	130	26	100-170	20
Sucker	5	1100	360	500-1500	33	<43	20	<20[b]-74	46
Chub	5	1100	380	820-1800	35	56	42	26-120	74

[a]Sediment expressed as dry weight basis and tissue expressed as fresh weight basis.

[b]Minimum detection limits for TBT and DBT were 12 and 20 ng/g (ppb), respectively.

water (25). According to the EPA, these values represent the highest concentration of TBT in water which would not present a significant risk to aquatic organisms and their uses. Although more TBT sensitive organisms were used to derive the final values, EPA listed acute and chronic values for some important Lake Tahoe species and related genera (Tables 10 and 11).

Phase I - Results from the initial phase indicated that four of the six lakes and eight of the ten marinas sampled had detectable TBT concentrations. These findings suggest that a large percentage of California's lakes with high boating densities may also have detectable TBT concentrations.

Phase II - Concentrations of TBT in water and sediment of Tahoe Keys Marina fall within the range detected in other marina areas of the United States and Canada. Concentrations of TBT in water ranged from 340 to 1400 ng/L and residues of TBT and DBT in Tahoe Keys Marina sediments ranged from 0.43 to 1.4 ng/g and from 0.40 to 1.1 ng/g (dry weight), respectively. Tributyltin concentrations of 800 to 1100 ng/L have been reported in areas of high boating activity in San Diego Harbor and Chesapeake Bay, respectively, while surveys of freshwater harbors in Canada have shown concentrations of TBT up to 560 ng/L (6). Sediment residue values in the Canadian harbors were similar to those found in the Lake Tahoe marina in that TBT was one to three orders of magnitude higher in sediment than in the water and DBT residues in sediment were equal to or higher than TBT residues (6).

Concentrations of TBT in water and residues in sediment decreased dramatically at the inlet to the marina and were non-detectable in the open waters of Lake Tahoe. However, fish caught in the open waters of Lake Tahoe contained up to 600 ng/g (fresh weight) TBT. Although data on fish tissue residues from other

Table 10. Acute toxicity values of tributyltin to freshwater aquatic animals (25).

Species	LC50[a]	Reference
	ng/L	
Amphipod, *Gammarus pseudolimnaeus*	3.7	Brooke et al. 1986
Rainbow trout (juvenile) *Salmo gairdneri*	3.9	Brooke et al. 1986
Rainbow trout (adult) *Salmo gairdneri*	25.2 (24 hr) 18.9 (48 hr)	Alabaster 1969 Alabaster 1969
Fathead minnow (juvenile) *Pinaphales promelas*	2.6	Brooke et al. 1986
Chinook salmon (juvenile) *Oncorhynchus tshawytscha*	1.5	Short and Thrower 1986

[a]Lethal concentration to 50% of a test population.

Table 11. Chronic toxicity values of tributyltin to freshwater aquatic animals (25).

Species	Limits	Chronic Value	Reference
	ng/L		
Cladoceran *Daphnia magna*	0.1-0.2	0.14	Brooke et al. 1986
Fathead minnow *Pimephales promelas*	0.15-0.45	0.26	Brooke et al. 1986

freshwater marinas were not available, TBT residues of 250 to 1190 ng/g for fish in Tahoe Keys Marina were similar to TBT residues in saltwater animals. Tissue residues from fish collected in various United States Navy harbors ranged from 120 to 3500 ng/g (fresh weight) TBT [data converted from ng/g (dry weight) total tin (2)].

The high TBT concentrations and residues detected at Tahoe Keys Marina can be attributed in part to the low water exchange rate caused by the marina's design. Access to the lake from the marina is via a long narrow channel which greatly limits the amount of mixing between the lake and marina waters. Water clarity within the marina is considerably less than in the lake proper thus limiting light penetration and inhibiting photolysis as a degradation pathway. Although microbial degradation could be an important factor within the marina, it is uncertain which bacteria possess this capability (26). With the high TBT concentrations in sediment, any TBT degraded in the water column could be replaced by desorption of TBT from the sediment. The rate of TBT desorption from sediment has been shown to be a function of the amount of agitation the sediment receives (8). It is not known if boat traffic in the marina produces sufficient water agitation to significantly influence the desorbtion rate of TBT from sediment. Additional factors influencing desorbtion would be boat size, boat speed, water depth and water temperature.

Recent legislation (Statutes of 1987, Chapter 539, Section 1 added chapter 2.5, Section 110 to Division 1.5 of the Harbors and Navigation Code) and amendments to the California Code of Regulations (3 CCR 6400, 6414, 6488, 6574, 6489, and 6900) enacted this year have greatly restricted the use of TBT paints. Tributyltin antifouling paint can now be applied only on boats over 25 meters in length or on any aluminum hulled boat and only by a certified applicator. It

also cannot be used on piers or fishing nets. Additional regulations that would establish maximum average release rates of TBT per square centimeter per day from paint are presently being developed.

V. CONCLUSIONS AND RECOMMENDATIONS

A significant hazard to aquatic life exists in the Tahoe Keys Marina and may exist in Lake Tahoe proper. Observed concentrations of TBT in the Tahoe Keys Marina exceed chronic toxicity values (0.03 to 0.10 ug/L) and approach lethal levels (0.30 to 4.0 ug/L)(25). Tissue residues in Lake Tahoe indicate fish were exposed to TBT. Tributyltin concentrations in the open waters of Lake Tahoe may be within chronic toxicity levels for aquatic organisms considering the bioconcentration factors for TBT of 4,000 to 30,000 (27) and therefore may represent a problem for aquatic biota.

Of primary concern in the marina's aquatic environment is the bioavailibility of TBT. According to Maguire et al. (28), any TBT in the water column is bioavailable and consequently has potential for toxic effects on aquatic life. Bioaccumulation of TBT in the food chain could be a serious problem especially to those organisms living and feeding in the benthos.

Even with the recent and planned regulations, the copolymer type paint already in use could continue releasing TBT for at least another five years (29). Given the present concentrations of TBT detected at Tahoe Keys Marina and the release rates of the paints presently in use, continued monitoring of the marina to guage the effectiveness of the regulations is strongly recommended. Yearly monitoring will provide necessary data on any observable degradation patterns in

the water and sediment, and provide information about TBT concentrations in the biotic community.

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APPENDIX I

SPECIES REPRESENTED IN THE BIOTA SAMPLES

Appendix I. Species, length and weight of animals collected on September 29, 1987 for determining TBT and DBT residues in tissue, Tributyltin Monitoring Study, Lake Tahoe, California. Not all fish were used in sample analysis.

Site No.	Fish	Total Length (mm)	Weight (g)
1	Tui chub	76	5.0
		87	6.7
		90	7.7
	Tahoe Suckers	47	1.1
		50	1.5
		43	0.8
		42	1.0
	Crayfish	95	23.2
		95	26.5
		100	30.5
		90	21.4
		110	45.2
		120	74.2
2	Tui chub	185	85.7
		140	37.6
		150	41.2
		135	32.5
		125	26.2
		210	143.7
		175	75.6
		160	49.8
		145	40.5
		180	85.1
		140	36.5
		140	39.0
		160	49.9
		145	41.1
		150	47.6
	Tahoe Sucker	220	126.5
		210	104.0
		220	101.8
		215	121.6
		205	96.7
		210	111.0
		205	100.4
		205	113.0
		240	149.3

Site No.	Fish	Total Length (mm)	Weight (g)
2	Tahoe Sucker	220	107.4
		220	104.9
		225	129.0
		210	99.0
		215	119.0
		220	127.7
		180	66.8
		170	53.0
		170	58.2
		210	105.4
		210	99.5
		165	49.5
		165	47.2
		170	56.8
		160	57.7
		175	54.6
		160	38.2
	Rainbow Trout	240	145.9
		230	251.2
		315	346.7
	Tui chub	150	37.4
		190	87.6
		195	100.9
		220	138.2
		140	136.2
		160	47.2
		180	74.5
		130	30.4
		200	108.7
		200	121.0
		190	90.0
		140	35.6
		140	34.5
		180	87.4
		205	117.4
		100	11.5
		90	10.6
		105	14.7
		105	11.6
		105	13.3
		100	11.8
		105	13.0
		95	9.5
		90	8.3

Site No.	Fish	Total Length (mm)	Weight (g)
3	Tui chub	90	9.2
		110	14.9
		80	6.1
	Tahoe Sucker	250	186.7
		220	105.2
		300	333.9
		260	209.9
		230	140.0
		210	111.6
		225	125.7
		200	97.2
		300	373.0
		260	124.5
		230	149.5
		205	100.7
		230	138.3
		265	221.6
		265	230.7
		170	54.3
		170	58.0
		170	50.0
		140	39.1
		150	40.7
		195	96.6
		160	47.6
		160	50.5
		160	45.4
	Rainbow trout	265	184.2
4	Tui chub	194	92.8
		190	98.1
		190	88.6
		190	87.5
		215	109.2
		215	142.5
		235	119.7
		150	34.0
		150	42.1
	Tahoe Sucker	330	347.6
		168	46.0
		160	36.3
		167	52.7
		218	119.3

Site No.	Fish	Total Length (mm)	Weight (g)
4	Tahoe Sucker	208	97.4
		150	36.8
		210	94.1
		220	131.6
	Brown trout	510	>1100
	Crayfish	130	37.6
		130	40.1
		130	59.0
		100	18.9
		120	33.5
		95	19.2

APPENDIX II

TRIBUTYLTIN AND DIBUTYLTIN CONCENTRATIONS IN WATER, SEDIMENT, AND BIOTA

Table II-1. Listing of butyltin concentrations in water samples collected from five monitoring stations in Lake Tahoe, September, 1987.

Sites	Depth in Meters	pH	Temp. °C	TBT	DBT
				ng/L	
Site 1					
Tahoe Keys Marina	Surface - 0.25	9.1	15	340, 410, 700, 1400	ND[a], 56, 92, 94
	Bottom - 3.66	9.3	15	600, 720, 790, 820	48, 80, 80, 94
Site 2					
Tahoe Keys	Surface - 0.25	8.9	17	89, 91, 140, 65	100, ND, ND, ND
Marina Inlet	Bottom - 3.66	7.2	17	41, 65, 84, 110	ND, ND, ND, ND
Site 3					
Lake Tahoe	Surface - 0.25	7.9	16	ND, ND, ND, ND	ND, ND, ND, ND
	Bottom - 1.50	7.9	17	ND, ND, ND, ND	ND, ND, ND, ND
Site 4					
Lake Tahoe	Surface - 0.25	7.9	15	ND, ND, ND, ND	ND, ND, ND, ND
	Bottom -13.00	7.5	16	ND, ND, ND, ND	ND, ND, ND, ND
Site 5					
Tahoe Keys Residential Marina Inlet	Surface - 0.25	8.9	17	ND, ND, ND, 31	ND, ND, ND, ND

[a]None detected; the minimum detectable limit for tributyltin and dibutyltin was 24 and 40 ng/L (ppt), respectively.

Table II-2. Listing of butyltin concentration in sediment samples collected from three monitoring stations in Lake Tahoe, September, 1987.

Sites	TBT	DBT
	ng/g, dry weight	
Site 1		
Tahoe Keys Marina	430, 490, 815, 1400	260, 400, 630, 1100
Site 2		
Tahoe Keys Marina Inlet	84, 130, 140, 210	ND[a], 40, 75, 200
Site 4		
Lake Tahoe	ND, ND, ND, ND	ND, ND, ND, ND

[a]None detected; the minimum detectable limit for tributyltin and dibutyltin was 12 and 20 ng/g, dry weight (ppb), respectively.

Table II-3. Listing of butyltin concentrations in biota samples collected from four monitoring stations in Lake Tahoe, September, 1987.

Sites	Sample Type	TBT	DBT
		ng/g, fresh weight	
Site 1			
Tahoe Keys Marina	Tahoe sucker	4800	840
	Tui chub	1300	500
	Crayfish	ND[a]	ND
Site 2			
Tahoe Keys	Tahoe sucker	1000, 1500, 480	28, 34, 22
Marina Inlet		860, (1700, 1400)[b]	ND, (38, 26)
	Tui chub	2000, 580, 2200	180, 80, 220
		840, (820, 960)	56, (ND, 60)
Site 3			
Lake Tahoe	Tahoe sucker	ND, 90, ND, 290, 14	ND, ND, ND, ND, ND
	Tui chub	380, 110, 360	30, 20, 38
		600, 290	72, 28
Site 4			
Lake Tahoe	Tahoe sucker	60, 290, ND	ND, ND, ND
	Tui chub	140, 460, 260	40, 70, 78
	Rainbow trout	100	ND
	Crayfish	ND	ND

[a]None detected; minimum detection limits for TBT and DBT were 12 and 20 ng/g, fresh weight (ppb), respectively.

[b]Figures presented in parentheses indicate sample split by CDFG laboratory.

APPENDIX III

LABORATORY ANALYTICAL METHODS

Water - Eight ml of 4% aqueous $NaBH_4$ was added to a 400-ml aliquot of sample water. The aliquot was extracted with 10 ml of petroleum ether for five minutes, and then the petroleum ether was passed through anhydrous granular Na_2SO_4. The extraction was repeated with another 10 ml of petroleum ether, and the extracts were combined. The extract was evaporated to 1 ml in a 50-ml tube with N_2 and gentle heat. The extract was transferred to a 10 ml tube with 2 ml of petroleum ether and gradually evaporated to 0.1 ml.

Fish - Ten g of homogenized fish tissue was added to 100 ml of H_2O, 15 g of NaCl, and 10 ml of HCl. The solution was blended with 50 ml of CH_2Cl_2 for two minutes and then vacuum filtered through No. 1 Whatman paper layered with acid washed celite. The organic layer was evaporated to 0.1 ml with a vacuum rotary evaporator at 40°C, and then the residue was dissolved in 1 ml of ethanol in a test tube. The hydride derivative was formed by adding 2 ml of 2.5% $NaBH_4$ in ethanol, shaken for one minute, and allowed to react at room temperature (20°C) for 10 minutes. Then, 5 ml of H_2O was added, shaken, and transferred to a separatory funnel. The test tube was rinsed with two, 5 ml portions of water and transferred to the separatory funnel.

Five g of NaCl and 5 ml of petroleum ether were added and shaken for five minutes. The petroleum ether extract was transferred to a 10 x 300 mm silica gel (5% deactivated) column. The sample was further eluted with 20 ml of petroleum ether in the column. The petroleum ether was then evaporated to 0.1 ml and then adjusted to 1.0 ml with isooctane.

Sediment - Twenty-five g of sediment was added to 100 ml of H_2O and 10 ml of HCl. The sample was then analyzed in the same manner as the fish tissue.

Conditions - The instrumental conditions on the Varian-Aerograph model 3700 gas chromatograph used for analysis were as follows:

Column: DC-200 on 800-100 mesh chromosrob W (AW-DMCS), Length: 183 cm.
I.D.: 2 mm
Detector Temperature: 250°C
Injector Temperature: 150°C
Column Temperature: 100°C x 3 minutes, 130°C x 1 minute,
160°C x 1 minute, 190°C for 3 minutes.
Carrier Flow: 30 ml/min.
Carrier Gas: N_2
Detector: FPD with 600 mm filter
Detection Limits: Water 24 ng/L TBT 40 ng/L DBT
Fish (wet) and Sediment (dry): 12 ng/g TBT, 20 ng/g DBT